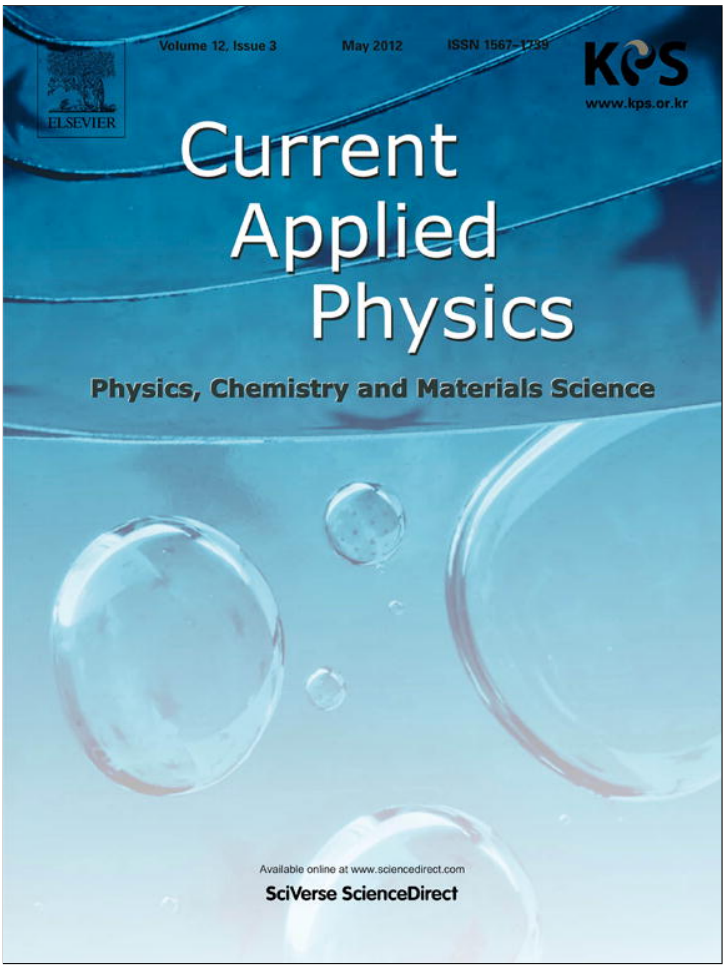

Current Applied Physics 12 (2012) 794–797

Contents lists available at SciVerse ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Theoretical study for magnetic effect in dissociative adsorption of oxygen to a platinum monolayer on Ni(110) surface

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ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form
27 October 2011
Accepted 9 November 2011
Available online 17 November 2011

Keywords:
Dissociative adsorption
Density functional theory
Magnetic effect

ABSTRACT

We investigate oxygen dissociative adsorption to a platinum monolayer on Ni(110) surface (Pt/Ni(110)) by density functional theory. We have shown that the activation barrier on Pt/Ni(110) is lower than that on a clean Pt(001) surface. This may be due to the effect of magnetization of Pt surface. The reason of decrease of activation barrier can be attributed to the flow of electrons from oxygen to platinum surface because the *d* orbitals have spin polarization at the Fermi level where the down spin *d* orbitals are unoccupied.

1. Introduction

Platinum-based transition metal alloys have shown to have greater activity than pure platinum for catalyzing oxygen reduction reaction [1]. Hence, clarifying the magnetic effect here becomes very crucial. In one of Kasai group's studies, using first principles calculations based on density functional theory (DFT), it is shown that in dehydrogenation of cyclohexane, catalytic reactivity of spin-polarized nickel is close to that of platinum [2]. In one of their next studies using DFT based first principles calculations, they have shown that on the Mg–H dissociation of MgH_2, Sc and Ni have the highest catalytic activities among the 3*d* transition metals (Sc–Zn) [3]. In their another study, they have shown that Pt monolayer on Fe(001) surface (Pt/Fe(001)) can be magnetized resulting to a reduction of activation barrier in O_2 dissociative adsorption in half [4] as compared to the case of bare platinum surface [5]. So as a next step, it is of importance to study how another magnetic material Ni influences this reaction by the same calculation method mentioned above. We consider O_2 dissociative adsorption on Pt/Ni(110) which has been experimentally fabricated [6].

2. Model and method

All calculations are based on spin-polarized density functional theory using the code Vienna *ab initio* simulation package (VASP) [7] employing generalized gradient approximation (GGA) for the exchange-correlation energy [8]. We treat ionic cores with projector augmented-wave (PAW) method [9]. We consider the model of a slab and an oxygen molecule (Fig. 1). The inter-atomic axis denoted by *r* is taken to be parallel to surface and the perpendicular distance of center of mass (CM) of oxygen molecule from the surface is expressed by *Z*. The slab consists of three atomic layers of fcc Ni(110) with a Pt monolayer on it. The unit cell of 4.98 Å × 10.56 Å × 19 Å has 18 Ni, 6 Pt and 2 O atoms. This unit cell is chosen so that there is no interaction between oxygen molecules of neighboring unit cells as well as between the oxygen molecules and the Ni–Pt slab of neighboring unit cells. The Brillouin zone is sampled by Monkhorst and Pack *k*-point sampling method with 6 × 4 × 1 k points. The calculation converges by a cutoff energy of 400 eV, which limits the plane wave basis set. The radii are taken to integrate the density to get the electron

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doi:10.1016/j.cap.2011.11.008

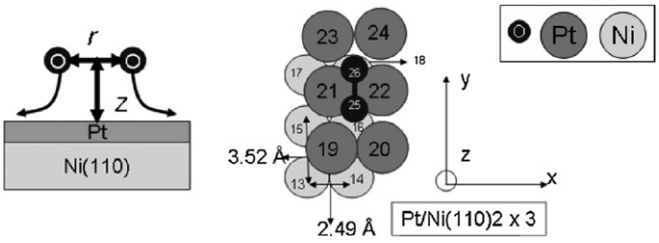

Fig. 1. Our system having a slab Pt/Ni(110) and an oxygen molecule. The slab consists of three atomic layers of fcc Ni(110) with a Pt monolayer on it. There are 18 Ni atoms (Ni1–Ni12 are not shown), 6 Pt atoms (Pt19–Pt24) and 2 O atoms (O25–O26) are in the unit cell.

number are as follows: for nickel 1.286 Å, for platinum 1.455 Å, and for oxygen 0.82 Å.

3. Results and discussions

We calculate total energy of the system; as we consider Born–Oppenheimer approximation the total energy of the system becomes the potential energy of the oxygen molecule. In Fig. 2, potential energy curve (PEC) – *i.e.*, relation between the distance of center of mass of O_2 from the surface Z (Å) and potential energy (eV) – is given for each inter-atomic distance r ($r = 1.2$–2.6 Å) of oxygen molecule. In this calculation we consider the initial state of reaction path (in Fig. 2 denoted by I) is at $Z = 3.25$ Å and $r = 1.2$ Å (we take this inter-atomic distance $r = 1.2$ Å from experimental data [10] which is the inter-atomic distance of oxygen molecule in equilibrium gas phase and consider that at $Z = 3.25$ Å the oxygen molecule is far from the surface). We can see that the activation barrier $E_a = 0.51$ eV is at $Z = 1.5$ Å. After it crosses this activation barrier the potential energy decreases and finally at $Z = 1$ Å the oxygen atoms are adsorbed (potential energy becomes minimum) where the binding energy is −0.77 eV. So the final state is that with $r = 2.6$ Å and $Z = 1.0$ Å (in Fig. 2 denoted by F). We consider this as dissociative adsorption because the distance between oxygen atom is quite long ($r = 2.6$ Å). The r and Z for final state ($r = 2.6$ Å, $Z = 1.0$ Å) of this system are almost same as that for final state ($r = 2.6$ Å, $Z = 1.10$ Å) of O_2 dissociative adsorption on Pt/Fe(001). The binding energy of oxygen with surface (i.e., potential energy at the final state) is −0.77 eV which is 80% bigger than the case of Pt/Fe(001) (−0.43 eV) [4]. Oxygen binds stronger on this surface than on Pt/Fe(001) surface. In this paper we do not reveal the mechanism of binding energy or

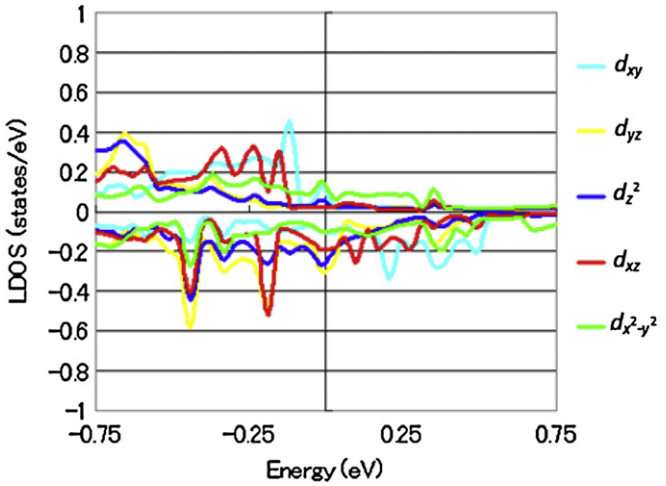

Fig. 3. Local density of states (LDOS) of Pt21 (see Pt21 in Fig. 1) in case of Pt/Ni(110) surface where there is no interaction of this surface with oxygen molecule. We see that the d orbitals have spin polarization at the Fermi level where the down spin d orbitals are unoccupied (for atomic configuration and x, y, z direction see Fig. 1). LDOS of down spin electron is multiplied by −1.

reasons of different value of binding energy of oxygen with Pt/Ni(110) and that with Pt/Fe(001). At present our investigation of this mechanism is ongoing considering these points, and hence reasons are not given in this paper.

In one [5] of the studies of Kasai group, it is shown that the activation barrier in the process of dissociative adsorption process of oxygen molecule on a clean Pt(001) surface is about ($E_a = 1.2$ eV). The activation barrier ($E_a = 0.51$ eV) for this system is almost the same as the case of Pt/Fe(001) ($E_a = 0.51$ eV) [4]. Both are less than half of the case at barrier a clean Pt(001) surface ($E_a = 1.2$ eV). This is due to magnetization of platinum. Fig. 3 shows local density of states (LDOS) of Pt21 (see Pt21 in Fig. 1) in case of Pt/Ni(110) surface where there is no interaction of this surface with oxygen molecule. We see that the d orbitals have spin polarization at the Fermi level where the down spin d orbitals are unoccupied (for annotations of atoms and x, y, z axes see Fig. 1).

Next we explain the effect of magnetism and how it can decrease the activation barrier, *i.e.*, how the O–O bond is broken. In Fig. 4 we see the electron number (valence orbital occupancy) of oxygen (a) as well as that of platinum (b). For four cases electron number are given: the initial state I ($r = 1.2$ Å, $Z = 3.25$ Å), two intermediate states denoted by INTER1 ($r = 1.4$ Å, $Z = 1.75$ Å) and

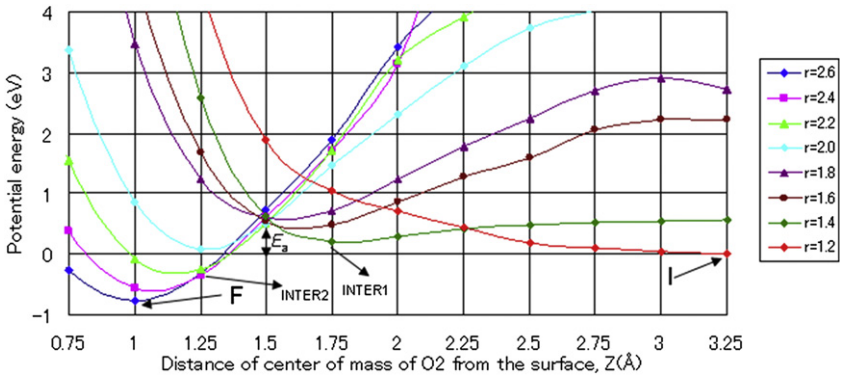

Fig. 2. Potential energy curve (PEC) for the dissociative adsorption process of oxygen molecule on Pt/Ni(110). Here relation between the distance of center of mass of O_2 from the surface Z and potential energy is given which is considered for each inter-atomic distance r ($r = 1.2$–2.6 Å) of oxygen molecule. The initial state I ($r = 1.2$ Å, $Z = 3.25$ Å), two intermediate states denoted by INTER1 ($r = 1.4$ Å, $Z = 1.75$ Å) and INTER2 ($r = 2.4$ Å, $Z = 1.25$ Å), and the final state F($r = 2.6$ Å, $Z = 1.00$ Å) of reaction path are also indicated. The activation barrier $E_a = 0.51$ eV is at $Z = 1.5$ Å. After it crosses this activation barrier the potential energy decreases and finally at the final state ($r = 2.6$ Å and $Z = 1.0$ Å) the oxygen atoms are adsorbed (potential energy becomes minimum) where the binding energy is −0.77 eV.

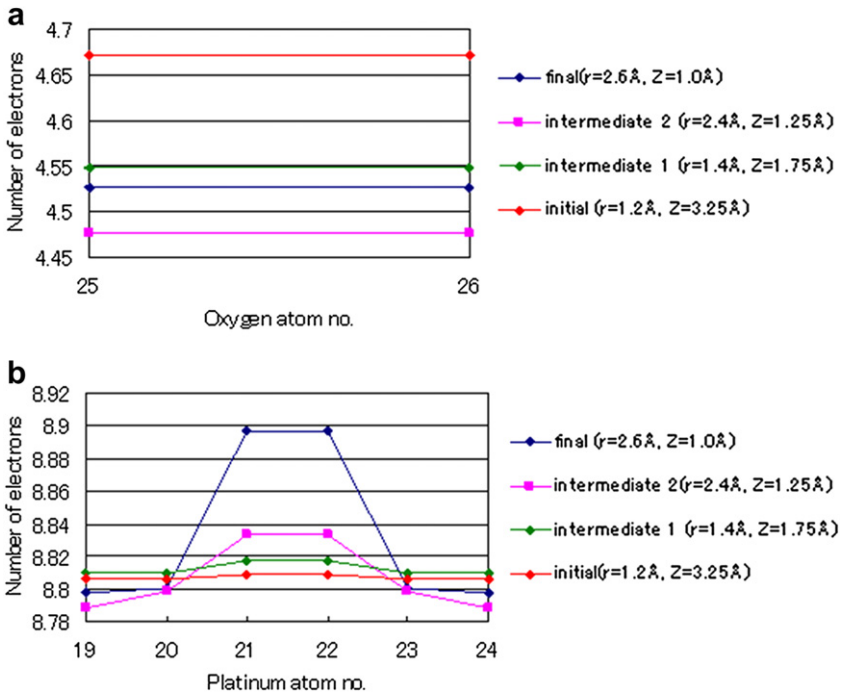

Fig. 4. Electron number of oxygen (O25–O26) and platinum (Pt19–Pt24) given in (a) and (b) respectively. For four cases electron numbers are given: the initial state ($r = 1.2$ Á, $Z = 3.25$ Á), two intermediate states denoted by INTER1 ($r = 1.4$ Á, $Z = 1.75$ Á) and INTER2 ($r = 2.4$ Á, $Z = 1.25$ Á), and the final state ($r = 2.6$ Á, $Z = 1.00$ Á).

INTER2 ($r = 2.4$ Á, $Z = 1.25$ Á), and the final state F($r = 2.6$ Á, $Z = 1.00$ Á). From initial state to INTER1 ($r = 1.4$ Á, $Z = 1.75$ Á) the total magnetic moment changes radically (see Fig. 5). The magnetic moment changes very little from INTER1 ($r = 1.4$ Á, $Z = 1.75$ Á) to state $r = 2.0$ Á, $Z = 1.50$ Á. The activation barrier is at this state ($r = 2.0$ Á, $Z = 1.50$ Á). At state INTER2 ($r = 2.4$ Á, $Z = 1.25$ Á) the magnetic moment again decreases. So we have chosen these two intermediate states between which the state ($r = 2.0$ Á, $Z = 1.50$ Á) with activation barrier.

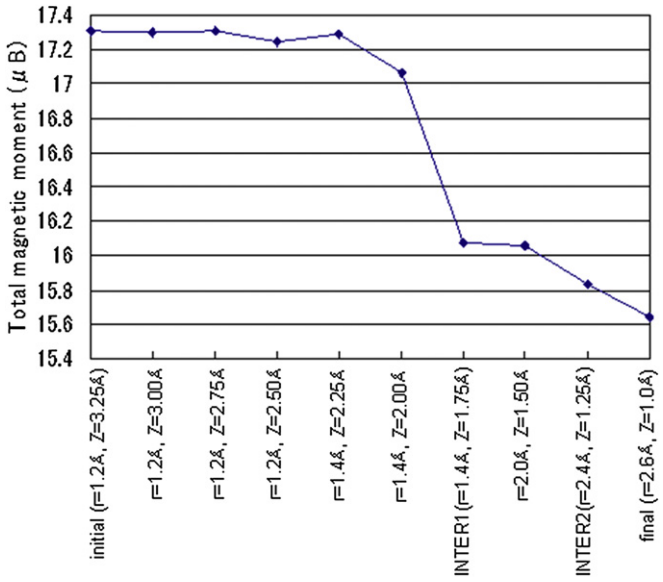

Fig. 5. Total magnetic moment for each state of the system. From initial state to INTER1 ($r = 1.4$ Á, $Z = 1.75$ Á) the total magnetic moment changes radically. The magnetic moment changes little from INTER1 to state $r = 2.0$ Á, $Z = 1.50$ Á. The activation barrier is at this state ($r = 2.0$ Á, $Z = 1.50$ Á). At state INTER2 ($r = 2.4$ Á, $Z = 1.25$ Á) the magnetic moment again decreases.

The electron number decreases for the both oxygen atom from the initial state to the intermediate state INTER2. But in the final state, again electron number increases. Also we can see that unlike the case of oxygen, electron number increases monotonously for Pt21 and Pt22 considering the above mentioned four states (Fig. 4 (b)). The magnetic moments of Pt21 and Pt22 decrease while those of Pt19, Pt20, Pt23 and Pt24 increase slightly. This is almost same as the case of O_2 dissociative adsorption on Pt/Fe(001) (Fig. 6 of Ref. [4]). The electrons move from oxygen to this platinum's unoccupied down spin *d* orbitals. And in the final state oxygen and platinum make bonding for which both electrons of oxygen and platinum increase. This flow of electrons of oxygen to *d* orbitals of platinum decreases the activation barrier in the reaction path, the dissociation of oxygen molecule becomes easier on Pt/Ni(110) than on clean Pt(100). In this case in the final state total spin of oxygen (O25–26) is has the same orientation of total spin of platinum (Pt19–24) which is different from the case of O_2 on Pt/Fe(001) where in the final state total spin of oxygen has opposite to total spin of platinum. If we look at the magnetic moment of Pt for the O_2 dissociative adsorption on Pt/Fe(001) and Pt/Ni(110) (Fig. 6 of this paper and Fig. 6 of Ref. [4]), we can see that for the case of Pt/Ni(110) magnetic moment of Pt decreases more than the case for Pt/Fe(001). This can be explained by LDOS of Pt in both systems (see Fig. 5(a) of Ref. [4] and Fig. 3 of this paper). In case of the LDOS of Pt in Pt/Fe(001), only down spin d_Z^2 orbital is more unoccupied. But in our case, in the LDOS of Pt in Pt/Ni(110) down spin d_Z^2 orbital is less unoccupied. However, all other down spin *d* orbitals are more unoccupied than the case of the LDOS of Pt in Pt/Fe(001). As a total, in the LDOS of Pt in Pt/Ni(110) down spin *d* orbitals are more unoccupied than the case of the LDOS of Pt in Pt/Fe(001). Hence, in Pt/Ni(110) Pt has more unoccupied down spin *d* orbitals compared to those of Pt/Fe(001). So electrons from oxygen occupy these *d* orbitals and electron number of Pt increases more than Pt during O_2 dissociative adsorption on Pt/Fe(001). As these occupy down spin *d* orbitals in both cases, magnetic moment decreases for the case of Pt/Ni(110) more than

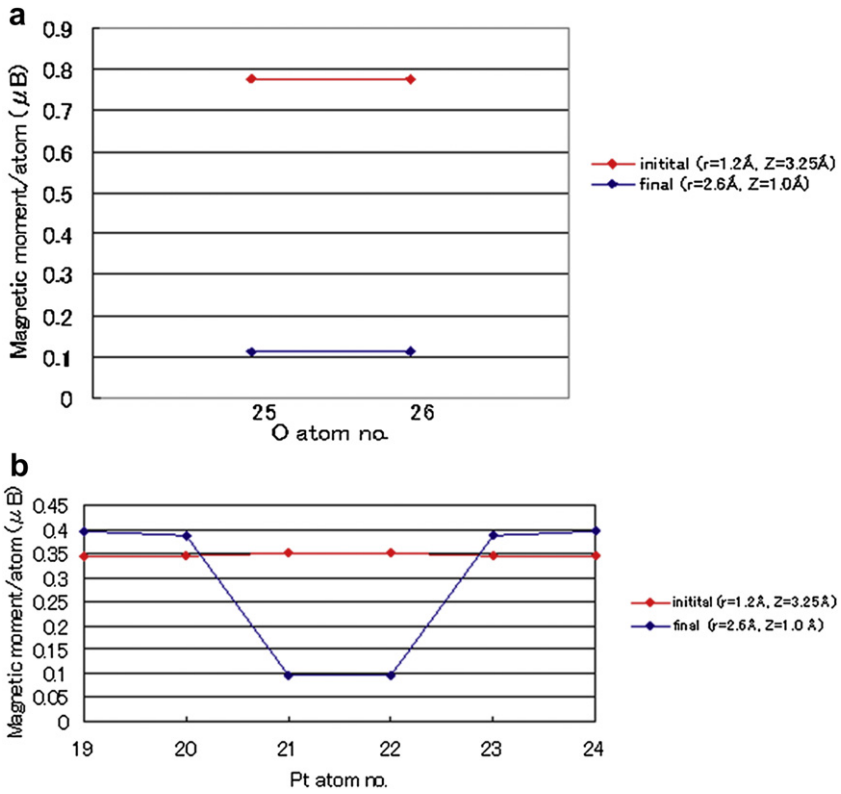

Fig. 6. Magnetic moment of oxygen (O25–O26) and platinum (Pt19–Pt24) given in (a) and (b) respectively. In oxygen the magnetic moment decreases as well as in Pt21 and P22 from the initial state (r = 1.2 Å, Z = 3.25 Å) to the final state (r = 2.6 Å, Z = 1.00 Å).

that of Pt/Fe(001). The magnitudes of LDOS for the unoccupied *d* orbitals those have *z*-axis components, *i.e.*, which come out from the surface (d_{yz}, d_Z^2 and d_{xz} orbitals), are bigger than those of the other two for which they can contribute to accept electrons from oxygen during its approach to surface.

4. Summary

We have investigated O_2 dissociative adsorption on Pt/Ni(110) surface by density functional theory. We have shown that the activation barrier on Pt/Ni(110) ($E_a \sim 0.51$ eV) is reduced compared to that on Pt(001) ($E_a \sim 1.2$ eV). This may be due to the effect of magnetization of Pt surface for which the *d* orbitals have spin polarization at the Fermi level where the down spin *d* orbitals are unoccupied. The flow of electrons of oxygen to these unoccupied orbitals of platinum decreases the activation barrier in the reaction path, the dissociation of oxygen molecule becomes easier on Pt/Ni(110) than on clean Pt(100).

Acknowledgments

This work is partly supported by Universiti Putra Malaysia, Ministry of Higher Education (MOHE), Malaysia through Fundamental Research Grant Scheme (FRGS) (Project Code: FRGS/1/11/ST/UPM/02/11), Surya College of Education (STKIP Surya), Indonesia and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) through Grants-in-Aid for Scientific Research on Priority Areas (Developing Next Generation Quantum Simulators and Quantum-Based Design Techniques), and through Grants-in-Aid for the 21st Century Center of Excellence (COE) Program "Core Research and Advance Education Center for Material Science and Nano-Engineering" supported by the Japan Society for the Promotion of Science (JSPS). Calculations were performed using the computer facilities of the Cybermedia Center (Osaka University), the Institute for Solid State Physics (ISSP) Supercomputer Center (University of Tokyo) and the Japan Atomic Energy Research Institute (ITBL, JAERI).

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